

"Averaged" statistical thermodynamics, energy equipartition and the third law

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Arguments are presented that the assumption, implicit to traditional statistical thermodynamics, that at zero temperature all erratic motions cease, should be dispensed with. Assuming instead a random ultrarelativistic unobservable motion, similar to *zitterbewegung*, it is demonstrated that in an ideal gas of classical particles the energy equipartition fails in a way that complies with the third law of thermodynamics.

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Introduction

Velocity cannot be measured. Readily measurable are positions and time intervals. Textbook definitions of velocity involve a limiting procedure in the definition of derivatives. Mathematically, such a procedure makes perfect sense; its operational meaning, however, is obscure. To clarify this statement, let me quote from Einstein's note [1] on brownian motion (in a loose translation):

"...Since an observer can never be aware of pieces of path passed in arbitrarily small intervals of time (regardless of the methods and means at his disposal), he will always accept as a momentary velocity some average velocity. It is clear, though, that the velocity determined in this way does not correspond to any objective property of the considered motion.."

Classical mechanics and, indirectly, classical statistical thermodynamics rely heavily on the notion of a Lagrangian. Being defined as a function of particle's coordinates and velocities, the Lagrangian cannot be measured, either. This circumstance by no means prevents its use in establishing the classical formalism; it is rather the interpretation of observations in terms of the theory where difficulties may be encountered.

One doesn't have to look far for examples of such difficulties. About the beginning of our century, one of the symptoms of the "crisis in physics" was that observations of the properties of thermal radiation were in conflict with energy equipartition – a rigorous result of classical statistical thermodynamics. To anyone sharing the ideas of Poincaré about the meaning of a physical theory [2], this could only mean that theory has been inconsistently applied to the interpretation of data; the physical community at that time, however, took the position that classical theory was wrong and needed modification, and eventually, quantum mechanics was born. It is not my purpose here to discuss the merits and shortcomings of quantum theory; in what follows I will rather try to explore the relevance of possible motions beyond the detectability limits of one's equipment to the issue of energy equipartition entirely within classical statistical thermodynamics.

The idea that there may exist motion beyond what can be readily observed is by no means new. Shortly after the discovery of Dirac's equation, Schrödinger pointed out that it predicts a curious phenomenon – ultrarelativistic erratic motion of the center of charge about the center of mass, that has been called *zitterbewegung* [3]. Since then, many aspects of both the quantum and classical versions of *zitterbewegung* have been studied (see e.g. [4]). However, to the knowledge of the present author, the implications of this irregular motion for thermodynamics have not received much attention so far. Hence, one way to define the purpose of the present work is studying the relevance of classical *zitterbewegung* for the issue of energy equipartition in classical statistical thermodynamics.

It should be noted of course, that equipartition of energy fails even in traditional statistical thermodynamics as soon as the motion becomes relativistic, and it does so at two counts. The relativistic relation between energy and velocity of a point particle does not possess the additivity property with respect to its three spatial degrees of freedom. Furthermore, the relativistic relation between energy and temperature involves particle's rest mass explicitly [5], hence in a relativistic gas at certain temperature, particles of different rest mass have different average energy. Therefore, it will be the purpose of the present work to explore the issue of energy equipartition in a situation where the apparent velocity is small enough compared to velocity of light, such as to suggest nonrelativistic treatment.

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Kinematics: Observable and hidden velocity

It should be clearly understood that the problem with the equipment mentioned in the introduction, is not merely a technical one but is connected with fundamental limitations of the theory. Indeed, it is well known that classical electrodynamics of an electron becomes self-contradictory whenever distances smaller than classical electron radius r_e and time scales smaller than $\tau_e = 2r_e/3c$ are involved [6]. Thus a prudent approach would separate electron's velocity β into a "mean" velocity

$$\beta_T(t) = \frac{1}{\tau_e} \int_0^{\tau_e} dt' \beta(t-t') = \frac{1}{c\tau_e} [\mathbf{r}(t) - \mathbf{r}(t-\tau_e)] \quad (1)$$

and the rest. Since we have no *a priori* knowledge about the actual velocity of the electron, we safely assume a relativistic situation. Relativistic kinematics imply

$$\beta_{\parallel} = \frac{\beta_T + \beta_{0\parallel}}{1 + \beta_0 \cdot \beta_T} \quad \beta_{\perp} = \frac{\beta_{0\perp} \sqrt{1 - \beta_T^2}}{1 + \beta_0 \cdot \beta_T} \quad (2)$$

where β_0 is the "unobservable" velocity and the \parallel and \perp components are with respect to β_T . From this expression one finds for the momentum

$$\begin{aligned} \mathbf{p} &= m_0 c \frac{\beta}{\sqrt{1 - \beta^2}} = \\ &= \frac{m_0 c}{\sqrt{1 - \beta_0^2}} \frac{\beta_T}{\sqrt{1 - \beta_T^2}} + \frac{m_0 c}{\sqrt{1 - \beta_0^2}} \frac{\beta_{0\parallel} + \beta_{0\perp} \sqrt{1 - \beta_T^2}}{\sqrt{1 - \beta_0^2}} \end{aligned} \quad (3)$$

and for the kinetic energy

$$E_k = m_0 c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right) = m_0 c^2 \left(\frac{1 + \beta_0 \cdot \beta_T}{\sqrt{1 - \beta_0^2} \sqrt{1 - \beta_T^2}} - 1 \right) \quad (4)$$

Lacking any knowledge of β_0 other than $\beta_0 \leq 1$, one can regard it as a random variable distributed isotropically. By virtue of Eqs.(3-4) momentum and energy become random variables, too. With this assumption the average momentum and the average energy turn out to be

$$\begin{aligned} \langle \mathbf{p} \rangle &= mc \frac{\beta_T}{\sqrt{1 - \beta_T^2}} \\ \langle E_k \rangle &= mc^2 \left(\frac{1}{\sqrt{1 - \beta_T^2}} - 1 \right) \end{aligned} \quad (5)$$

where the average mass is given by

$$m = \left\langle \frac{m_0}{\sqrt{1 - \beta_0^2}} \right\rangle \quad (6)$$

Apparently, the average momentum and energy have the customary dependence on the mean velocity. The only effect of the unobservable velocity on them is that the particle's mass appears to be larger. If observer's equipment can only measure average momenta and energy, no experiment can reveal either the presence of β_0 or the value of m_0 . This situation radically changes as soon as one considers fluctuations.

Fluctuations of energy and apparent temperature

Within statistical thermodynamics, the temperature θ can be related to the dependence of the energy fluctuations on the average energy [7]:

$$-\frac{\partial \overline{E}}{\partial \theta^{-1}} = \overline{E^2} - \overline{E}^2 \quad (7)$$

where the overbar indicates thermal averaging. One way to look at this relation is as a statistical definition of temperature, consistent with the first and second principles of thermodynamics. For example, if energy is distributed with probability density involving *only one parameter* with dimensions of energy $F(E/E_0)$ (the canonical distribution obviously belongs to this class):

$$\begin{aligned}\overline{E} &= \frac{\int dE E F(E/E_0)}{\int dE F(E/E_0)} = E_0 \frac{\int dx x F(x)}{\int dx F(x)} \equiv a E_0 \\ \overline{E^2} &= \frac{\int dE E^2 F(E/E_0)}{\int dE F(E/E_0)} = E_0^2 \frac{\int dx x^2 F(x)}{\int dx F(x)} \equiv b E_0^2 \\ \overline{E^2} - \overline{E}^2 &= \left(\frac{b}{a^2} - 1\right) \overline{E}^2 \equiv d \overline{E}^2\end{aligned}$$

where a, b and d are non-negative dimensionless constants depending on the particular form of the distribution function. Plugging the result of the last row above into Eq.(7) and solving with boundary condition $\lim_{\theta \rightarrow \infty} \overline{E} = \infty$, we obtain the familiar relation

$$\overline{E} = \frac{\theta}{d} \quad (8)$$

For the canonical distribution d is, of course, equal to $2/N$ where N is the number of degrees of freedom, and Eq.(8) expresses the energy equipartition property of classical statistical thermodynamics.

The relevance of the above definition of temperature to our discussion becomes apparent when we allow β_T above to be a subject of thermal fluctuations, statistically independent from the fluctuations of β_0 . In other words, we shall be interested in exploring the effects of the unobservable motion on the statistical properties of the observable one. Straightforward manipulation using Eq.(4) and the isotropy of β_0 yields, with $\gamma_T \equiv (1 - \beta_T^2)^{-1/2}$

$$\langle E_k^2 \rangle = \frac{4 \langle m^2 \rangle c^4 - m_0^2 c^4}{3} (\gamma_T - 1)^2 + 2 \frac{\langle m^2 \rangle c^4 - m_0^2 c^4}{3} (\gamma_T - 1)$$

Combining this with Eq.(5) and performing thermal averaging, we arrive at

$$\begin{aligned}\langle \overline{E_k^2} \rangle - \langle \overline{E_k} \rangle^2 &= \\ &= \frac{4 \langle m^2 \rangle - m_0^2}{3m^2} (mc^2)^2 (\gamma_T - 1)^2 - \langle mc^2 \rangle^2 (\gamma_T - 1)^2 + \\ &+ 2 \frac{\langle m^2 \rangle - m_0^2}{3m^2} mc^2 \left[mc^2 (\gamma_T - 1) \right]\end{aligned} \quad (9)$$

Eq.(9) reveals two distinct effects of the presence of the unobservable velocity β_0 . First, the coefficient $\frac{4 \langle m^2 \rangle - m_0^2}{3m^2}$ appears whereas in the absence of β_0 one would have a unit factor instead; and second, the whole last term in the right-hand side of Eq.(9), is absent in the traditional approach.

At this point it is convenient to make two further assumptions concerning the statistics of the unobservable velocity. First, given the general validity of statistical thermodynamics, we can safely assume that β_0 is distributed according to the relativistic Maxwell law with some temperature θ_0 . Simple calculation then produces

$$\begin{aligned}m &\equiv \langle m \rangle = m_0 \left[\frac{3}{\alpha} + \frac{K_1(\alpha)}{K_2(\alpha)} \right] \\ \langle m^2 \rangle &= m_0^2 \left[\frac{12}{\alpha^2} + 1 + \frac{3K_1(\alpha)}{\alpha K_2(\alpha)} \right]\end{aligned}$$

where K_n is a modified Bessel function of the second kind and $\alpha \equiv m_0 c^2 / \theta_0$. Second, let us take θ_0 large enough such as to have $\alpha \ll 1$. This means that the bare mass m_0 is assumed small compared to the apparent mass $\langle m \rangle$. For the time being let us consider this second assumption simply as a means for simplifying the resulting expressions. Thus, we calculate

$$\frac{\langle m^2 \rangle}{m^2} = \frac{4}{3} + O(\alpha^2)$$

and rewrite Eq.(9) in lowest (zeroth) order of α as

$$\begin{aligned}
& \langle \overline{E_k^2} \rangle - \langle \overline{E_k} \rangle^2 = \\
& = \left[\left(\frac{4}{3} \right)^2 (1 + \varkappa) - 1 \right] \langle \overline{E_k} \rangle^2 + \frac{2}{3} \times \frac{4}{3} \langle mc^2 \rangle \langle \overline{E_k} \rangle \\
& \varkappa \equiv \frac{(\gamma_T - 1)^2}{(\gamma_T + 1)^2} - 1 \in [0, 1]
\end{aligned} \tag{10}$$

Using this in Eq.(7), we can ascribe an apparent temperature associated with $\langle E_k \rangle$, i.e. with the observable velocity β_T . Requiring, as above, $\lim_{\theta_T \rightarrow \infty} \langle \overline{E_k} \rangle = \infty$, solving the differential equation, and defining $\varepsilon_0 = 4/3 \langle mc^2 \rangle$, we easily obtain

$$\langle \overline{E_k} \rangle = \frac{2/3}{\left(\frac{4}{3} \right)^2 (1 + \varkappa) - 1} \frac{\varepsilon_0}{\exp\left(\frac{\varepsilon_0}{3\theta_T/2}\right) - 1} \equiv \frac{1}{\tilde{\varkappa}} \frac{\varepsilon_0}{\exp\left(\frac{\varepsilon_0}{3\theta_T/2}\right) - 1} \tag{11}$$

Now, this is a very curious result that needs few comments. The first one concerns our definition of ε_0 . The factor $4/3$, appearing in connection with electron mass, has aquired certain notoriety in the context of a discussion about the electromagnetic contribution to the mass [8]; its origin however is most clearly explained in relativistic thermodynamics: in relativistic systems the quantity that, together with the three components of momentum, forms a 4-vector, is the enthalpy rather than the energy [9]. Now it is easy matter to verify that, in zeroth order of α , the enthalpy per particle is exactly $4/3$ times the energy per particle [5], coinciding with our ε_0 from above.

The second comment concerns the behaviour of an ideal gas of classical particles with $\beta_0 \neq 0$. It is well known that traditional ideal gas, where β_0 is absent, is out of touch with the third law of thermodynamics; actually it is true for every system satisfying the energy equipartition theorem. Historically, energy equipartition failure has been first demonstrated for blackbody radiation, and has been explained by introducing the notion of quanta. Thus, the fact that experimentally observed thermodynamic systems obey the third law of thermodynamics and violate energy equipartition theorem is usually regarded as a proof of the quantum nature of those systems. In a marked contrast to this, our Eq.(11) implies the following expression for the specific heat capacity of an ideal gas of classical particles with $\beta_0 \neq 0$:

$$c_V \equiv \frac{\partial \langle \overline{E_k} \rangle}{\partial \theta_T} = \frac{2}{3\tilde{\varkappa}} \frac{\varepsilon_0^2}{\theta_T^2} \frac{\exp\left(\frac{\varepsilon_0}{3\theta_T/2}\right)}{\left[\exp\left(\frac{\varepsilon_0}{3\theta_T/2}\right) - 1\right]^2} \tag{12}$$

whereas for traditional ideal gas $c_V = 3/2$ holds. Letting the apparent temperature θ_T go to zero, we observe that c_V defined by Eq.(12) goes to zero, too. Now this behaviour is just the crucial aspect of the third law [10], hence the presence of the β_0 causes a failure of energy equipartition in a way that makes our classical system compliant with the third law of thermodynamics.

As a last comment, a remark concerning the high-temperature behaviour of Eqs.(11,12) is in order. For $\theta_T \rightarrow \infty$ we have

$$\langle \overline{E_k} \rangle \simeq \frac{1}{2\tilde{\varkappa}} 3\theta_T \quad c_V \simeq \frac{3}{2\tilde{\varkappa}}$$

This is about as far as we can go without further information about the distribution of β_T . Assuming for a moment relativistic Maxwell distribution for β_T , we find $\varkappa = 1/3$ and $\tilde{\varkappa} \simeq 2.06$. Thus, at high temperature an ideal gas of particles with ultrarelativistic β_0 would appear, due to the factor $\tilde{\varkappa}^{-1}$, like traditional ideal gas with about half of its degrees of freedom "frozen" and not contributing to its heat capacity. This, as well as the form of Eqs.(11,12) is curiously reminiscent of the properties of an ideal Bose-Einstein gas.

Discussion

A meaningful physical theory should possess certain "stability" of its predictions with respect to assumptions that cannot be experimentally tested [11]. One such assumption in classical statistical thermodynamics is that the apparent velocity of a particle is identical to its actual velocity. Whether this is true or not is an issue that cannot be settled down within classical theory, due to the limitations to scales larger than classical electron radius and corresponding time intervals, inherent to classical electrodynamics. In traditional classical physics this assumption, in a form stating

that at zero temperature all erratic motion ceases, is always implicitly done. In the case of thermodynamics of classical electromagnetic radiation and charged harmonic oscillators, it has been shown that dispensing with it not only doesn't inflict basic thermodynamic principles, but even makes possible an entirely classical understanding of the phenomenology of blackbody radiation [12]. In a more general context, admitting the existence of a Lorentz-invariant classical random electromagnetic field at zero temperature results in an interesting classical theory, called "Stochastic Electrodynamics", which has proven capable of dealing with a number of phenomena, usually believed to belong to the quantum realm, but still lacks the generality of quantum theory and possesses problems of its own (for a review with extensive references, see [13]). This, combined with the results of the present work, clearly demonstrates the instability of the predictions of traditional classical thermodynamics with respect to the assumption of the absence of erratic motion at zero temperature. It, therefore, should be purged from the theory, and it is our conjecture that, without it, classical statistical thermodynamics would provide comprehensible description of all phenomena currently believed to require quantum treatment. Whether this is true, and how this could be done, remains to be elaborated on.

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